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**(57) Abstract**

Particle compositions are described comprising certain metal halides in combination with a strengthening agent. The addition of the strengthening agent to a metal halide particle increases the particle's strength thereby reducing breakage on impact and during handling. When used as a vaporizable metal halide fill in discharge lamps, the particle strength is increased without significantly altering the spectral and electrical characteristics of the lamp. Methods of making the particles and arc tube containing the particulates are also disclosed.

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STRENGTHENED METAL HALIDE PARTICLES AND IMPROVED  
LAMP FILL MATERIAL AND METHOD THEREFOR

BACKGROUND OF THE INVENTION

Metal halides have a variety of uses, many of which require high purity. They are easily contaminated by water and oxygen and are generally handled in dry boxes.

One of the primary uses of metal halides is as a fill material in the arc tube of electric gas discharge lamps. Such lamps use a variety of fill materials including rare gases, metals, mercury amalgams and metal halides, and the proper operation of such lamps requires that these lamp fill materials contain less than 200 ppm oxygen, preferably less than 50 ppm, and less than 100 ppm hydrogen, preferably less than 20 ppm, and desirably less than 5 ppm.

The proper operation of such lamps also requires that the fill materials be inserted in precisely measured quantities during the fabrication of the lamps. Of particular concern is the vaporizable metal halide fill, generally in the form of pellets or particles. These metal halides determine the electrical and spectral characteristics of a lamp, and it is well known to select particular metal halides and their relative concentrations both to give light of a desired color and to impart desired electrical characteristics to the arc.

A typical metal halide arc tube contains a mixture of metal halides dosed as one or more spherical particles or a cylindrical pellet of precise composition and size.

Various methods are known for manufacturing both spherical uniform composition metal halide particles as shown in Figure 1 and pellets (i.e., physically aggregated metal halides) as shown in Figure 2.

If uniform composition and size is desired, the particles of Figure 1 may be made by the apparatus schematically illustrated in Figure 3, such apparatus and the manufacturing processes being of the type described, e.g., in the Anderson U.S. Patent No. 3,676,534 dated July, 1972 and assigned to the assignee of the present invention, the content of which is hereby incorporated by reference.

In the process described in the Anderson patent, uniformly sized particles of metal halide mixtures are formed by forcing a homogeneous melt through an orifice of known diameter at a known velocity and acoustically or electromechanically breaking the molten jet into controlled lengths.

Using this process of controlled jet break up, a mixture of  $\text{DyI}_3$ ,  $\text{NdI}_3$ , and  $\text{CsI}$  with the  $\text{CsI}$  concentration greater than approximately 35 mole percent, forms particles which are quite weak, if particles are formed at all. These compositions typically have compressive breaking strengths, as measured by crushing a particle between two flat surfaces, of about 25 grams or less.

An alternative process described in the Anderson U.S. Patent No. 4,201,739 dated May, 1980 and assigned to the assignee of the present invention, the content of

which is hereby incorporated by reference. In that Anderson patent, particles are formed by the controlled wetting of an orifice which allows the dripping of molten metal halide spheres of a larger diameter.

Additionally, powders of a variety of metal halides may be aggregated by pressing into a cylindrical pellet or compacted tablet such as illustrated in Figure 2 in a conventional mechanical device. (See, e.g., Friedrich U.S. Patent No. 4,248,584). Finally, pellets for use in metal halide arc tubes have been produced by casting or by combining melting and pressing. (See e.g., Schaller U.S. No. 3,729,247).

It is known that the melting of metal halide mixtures can produce a homogeneous liquid, which if jetted, dropped, cast or pressed as described above, will produce Particles having a bulk composition that is the same as the original molten mixture. When a homogeneous liquid is rapidly frozen and ground into a powder it is in a suitable form for being pressed into a cylindrical or tablet shape.

For efficiency of manufacture, uniformity of dosage, and consistency of the electrical and spectral characteristics of the lamps dosed, it is advantageous to combine several metal halides into a single particle or pellet. Each of these doses must have uniform composition to ensure consistent color and arc characteristics within the lamp and are dosed into the lamp arc tube by various mechanical schemes.

However, the metal halide particles and pellets, without regard to shape, (hereinafter referred to individually and collectively as "Particles") are frequently subjected to considerable mechanical abuse in the various manufacturing, handling, and dosing processes. To routinely withstand the rigors of manufacture, handling, shipping, and dosing the breaking strength of the metal halide particle needs to be greater than about 100 grams as measured by crushing a particle between two parallel surfaces, or through the use of a three point bend test. Certain metal halide mixtures do not form particles or pellets strong enough to withstand this mechanical abuse.

In addition, certain metal halide compositions can not readily be united into a single Particle. For example, a mixture containing iodides of dysprosium, neodymium, and cesium with a cesium content above approximately 35 mole percent could not be pressed into a solid pellet.

One reason for the fragility of metal halide mixtures is phase transformations. For example, a large volume change resulting from freezing of the particle may cause the particle to be in tension on its surface and under compression in its liquid interior. The result is often a particle with a large residual stress, which stress may lead to cracks or cleavage.

Other reasons for the fragility of the particle include the formation of weak and brittle intermediate

phases, excessive numbers of cracks or voids, or both, and growth in preferred orientations that are weak.

Breakage on impact may be a significant problem in the formation of particles which are formed by a process in which the particles fall through a cooling tower and impact either the collecting vessel or previously collected particles. Depending on the need for spherical particles, significant waste may thus result in the formation and in the subsequent shipping and handling of such particles.

Without regard to the shape of the Particle being dosed, the implementation of the dosing of lamps with the desired metal halides in the desired quantity to obtain a desired color has heretofore suffered from the imprecision resulting from Particle breakage. Whether the fill is dosed by count or by volume, breaking of the fragile Particles during manufacture, shipment, handling and dosing may result in lamps with electrical and spectral characteristics other than those desired, and variation from lamp to lamp.

In addition to the variations which result from overdosing and underdosing of the lamps, breakage of the Particles may clog the dosing apparatus, disrupting the manufacturing process and wasting an expensive component of the lamps.

Because of the fragility of certain metal halide compositions, there is a great need for a strengthening agent that will not deleteriously affect the intended use

of the Particle, e.g., in a lamp the agent must not significantly vary any of the arc characteristics, chemically react with the lamp electrodes, if present, or the walls of the arc tube.

It is thus highly desirable to strengthen the fragile Particles without negatively impacting the electrical and spectral characteristics of the lamp or the various arc tube components such as electrodes.

Attempts to strengthen metal halide particles without the addition of a strengthening agent have been partially successful. Annealing metal halide particles has produced a slight increase in the strength of certain particles, but the success of this procedure has been limited to relatively few materials. By controlling the freezing rate of metal halide particles, a few fragile compositions have been manufactured with improved strengths that allow them to be mechanically dosed. However, neither annealing nor control of freezing rate is universally applicable to metal halides.

It is accordingly an object of the present invention to provide a novel strengthening agent for metal halide Particles, a novel process for strengthening metal halide Particles, and novel compositions of Particles.

Another object of the present invention is to provide a novel composition for, and method of making, vaporizable metal halides useful in gas discharge lamps.

Yet another object of the present invention is to provide an strengthening agent for a vaporizable lamp



fill which increases the breakage resistance of the material without significantly affecting the electrical and spectral characteristics of the lamp.

A further object of the present invention to provide a novel breakage resistant composition for metal halide Particles having particular utility as lamp fill material for metal halide lamps.

These and many other objects and advantages of the present invention will be readily apparent to one skilled in the art to which the invention pertains from a perusal of the claims, the appended drawings, and the following detailed description of the preferred embodiments.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of one embodiment of the break resistant particle of the present invention.

Figure 2 is a schematic representation of one embodiment of the break resistant pellet of the present invention.

Figure 3 is an illustration of an apparatus for manufacturing the particles with improved breakage resistance.

Figure 4 is a schematic representation of an arc tube incorporating the Particles of the present invention.

Figure 5 is a graph of experimental test results showing the optimization of the effects on breaking

strength by the addition of the strengthening agent to the parent metal halide.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

While of utility with metal halides generally, the present invention may be easily understood in the embodiment of a vaporizable metal halide fill for use in gas discharge lamps to determine the color characteristics of the lamp. Such fill material may take the form of particles as shown in Figure 1 or pellets as shown in Figure 2. Such Particles may be fragile and susceptible to breakage during manufacture, handling, shipping and dosing to produce the arc tubes for gas discharge lamps such as illustrated in Figure 4.

Particles suitable for use as lamp fill material typically consist of combinations of various metal halides such as dysprosium iodide and neodymium iodide, typically produced as spheres having an average diameter between about 100 and about 3,000 microns, and preferably between about 150 and about 1,200 microns. However, such particles may be produced in the dripping process described above with a diameter between about 1600 and about 3000 microns, preferably between about 1750 and about 2500 microns.

Such lamp fill material may consist of a parent metal halide (alone or in various combinations) from the group consisting of iodides, bromides and chlorides of one or more of the following metals:

Li, Na, K, Rb and Cs in Group 1,  
Mg, Ca, Sr and Ba in Group 2,  
Sc, Y and La in Group 3,  
Ti, Zr and Hf in Group 4,  
Nb and Ta in Group 5,  
Mn in Group 7,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
As, Sb and Bi in Group 15,  
Te in Group 16,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and  
Th in the Actinide Series.

Preferably, lamp fill material may consist of a  
parent metal halide (alone or in various combinations)  
from the group consisting of iodides and bromides of one  
or more of the following metals:

Li, Na, K, Rb and Cs in Group 1,  
Sc, Y and La in Group 3,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,

Sn and Pb in Group 14,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and  
Th in the Actinide Series.

It has been found effective to add a small amount of a strengthening agent from Group 11 (Ag, Cu and Au) consisting of one or more the following metal halides  $\text{AgI}_x$ ,  $\text{AgBr}_x$ ,  $\text{AgCl}_x$ ,  $\text{CuI}_x$ ,  $\text{CuBr}_x$ ,  $\text{CuCl}_x$ ,  $\text{AuI}_x$ ,  $\text{AuBr}_x$  and  $\text{AuCl}_x$ , and preferably AgI, AgBr, CuI and CuBr, where  $0.95 < X < 1.05$ , and preferably  $0.99 < X < 1.01$ .

The addition of a strengthening agent is not limited to a particular Group of metal halides or to any mixture of metal halides. For example, it has been found that the addition of copper monoiodide (CuI) or silver monoiodide (AgI), approximately 1.5 mole percent, to a molten metal halide mixture which otherwise produces weak spheres, formed particles typically having a breaking strength 2 to 20 times stronger than those formed without the addition of the strengthening agent.

However, an optimum modifier concentration probably exists for each particular metal halide composition. For example, the addition of 5 mole percent AgI overmodified a mixture of dysprosium, neodymium and cesium iodide causing the mixture to return to a powder.

Copper and silver iodides have been found effective as strengthening agents. The preferred compounds are silver iodide and copper iodide because of their ability to bind iodide mixtures and iodide-bromide mixtures and

because their strong emissions are not in the visible wavelengths. Gold iodide and gold halides may also act as strengthening agents, and gold iodide also does not have any significant emission lines in the visible region of the spectrum.

Table 1 shows the color rendition index (CRI), operating voltage, lumens, and color temperature of a metal halide mixture with 2.3 mole percent AgI in the dosed material and the same lamp characteristics in a control lamp. For different metal halide compositions there are slight variations, on the order of 2 percent, either up or down in the operating parameters of the finished metal halide lamp. Silver iodide has the effect of slightly broadening the arc of the lamp, but has no significant effects on CRI, lumens, and other electrical and spectral properties of the arc.

#### 100 WATT LAMPS WITH AND WITHOUT AgI IN DOSE

##### DyI<sub>3</sub>-NdI<sub>3</sub>-CsI Doses

Number	Dose	Operating Voltage	Lumens	Color Temperature	CRI
1	DyNdCsI	98.3	6403	6470	92.36
2		98.6	6330	6429	93.32
3		108.9	6631	6143	88.82
4		99.4	6416	5155	94.83
5	DyNdCsI+	104.3	6038	6673	93.93
6	2.3 mole percent	110.4	6258	6369	94.56
7	AgI	106.4	6350	5728	94.99

Table No. 1

The use of silver iodide and copper iodide as the strengthening agent for metal halide Particles, in amounts from about 0.25 to about 5 mole percent, preferably from about 1.0 to about 1.5 mole percent, are preferred for use in metal halide lamps since the color rendition index and other spectral and electrical measurements of the lamp made from a strengthened particle are not significantly changed.

A further advantage in the use of silver iodide is that its vapor pressure is relatively low at the operating temperature of the metal halide arc tube. A low vapor pressure will help to prevent the silver iodide from becoming an important part of the metal halide arc, particularly the emission spectrum. Moreover, it is known that silver and silver iodide are benign as to an attack on the silica arc tube of a metal halide lamp, i.e., they do not devitrify or etch the walls of the arc tube because silver oxide ( $\text{Ag}_2\text{O}$ ) is much less stable than silica ( $\text{SiO}_2$ ), and the addition of silver metal to the arc tube dose does not accelerate the decomposition of iodides such as sodium iodide ( $\text{NaI}$ ) and neodymium iodide ( $\text{NdI}_3$ ) in the lamp. (See the Chang European Patent No. 645 799 A1 and U.S. Patent No. 5,483,244).

In one embodiment, a small percentage, by weight, of a metal halide additive is added to the "parent" metal halide prior to formation of the particle or pellet. The percentage of the additive is preferentially chosen such that the strength of the resulting Particle is increased

without significantly impacting the electrical or spectral characteristics of the lamp. Amounts of additive less than approximately two percent of the Particle weight have been found to advantageously increase the strength of the Particle by a factor of four without significantly impacting the electrical or spectral characteristics of the lamp.

In another embodiment, the addition of a small amount of copper monoiodide (CuI) or silver monoiodide (AgI), approximately 1.5 mole percent, to a molten metal halide mixture which otherwise produces weak spheres, typically produced particles having a breaking strength 2 to 20 times stronger than those formed without the addition of a modifier.

The following are specific examples illustrating the beneficial effects of the strengthening agent.

EXAMPLE 1: A mixture of 75 mole percent sodium bromide and 25 mole percent sodium iodide was jetted as described in the Anderson U.S. No. 3,676,534 produced a powder that cannot be considered as spheres and which is devoid of breaking strength. The addition of 1.5 mole percent silver iodide (AgI) to the same sodium iodide-sodium bromide melt prior to jetting produced spheres having a breaking strength of 380g on average, i.e., generally between about 150g and 450g.

EXAMPLE 2: The procedure of Example 1 was repeated with a melt consisting of halides of sodium, scandium, and lithium and produced spheres having a breaking

strength of 50g. When the procedure was repeated with the addition of 1.5 mole percent AgI, spheres were produced having a breaking strength between about 100g and about 200g, averaging about 180g.

EXAMPLE 3: The procedure of Example 1 was repeated with the melt consisting of a mixture of tin, thallium and sodium halides. The strength of the particles without annealing was approximately 50g. When annealed, the strength of the particles increased to about 170 g. When the procedure was repeated with the addition of 1.5 mole percent AgI, the breaking strength of the particles was in the range 400g - 500g.

EXAMPLE 4: The procedure of Example 1 was repeated six times with a range of silver iodide additions to the melt. As shown in Fig. 5, the breaking strength of the jetted particles without the addition of the strengthening agent was about 38g. The breaking strength increased to a maximum of about 175g in the neighborhood of 2.0 - 2.5 mole percent AgI, with further increases in AgI reducing the breaking strength of the particles.

To some extent, breaking strength is a function of the size of the Particle, and Particles having a weight between 1.0 and 2.5 mg have generally been used. With such Particles, a breaking strength greater than 100g is generally required for handling in the dosing of lamps. However, Particles have been produced having a breaking strength of 250g, 350g and even 500g and higher. This generally represents an increase by a factor of at least



generally represents an increase by a factor of at least 1.25, but an increase by a factor of 5, and even 10 to 20, has been experimentally obtained.

The precise mechanism by which the increased breaking strength is achieved may not be fully understood. One probable mechanism for strengthening metal halide spheres by the addition of silver, gold, and copper halides is the ability of these halides to prevent supercooling during freezing. Rapid freezing may be one reason that metal halide structures are weak. In some cases, silver, copper and gold halides may behave as a nucleation site for solidification and prevent large supercooling and the subsequent very rapid solidification from occurring.

A second possible mechanism by which the strengthening occurs is the ability of these strengthening agents to cause solidification in "strong" crystallographic directions rather than in "weak" crystallographic directions. Silver iodide may enhance crystallographic growth in "strong" directions.

A third possible mechanism observed in certain metallic alloys is due to adsorption of the strengthening agent onto one of the phases and the alteration of the normal solidification and growth of this constituent.

In the present invention the modification mechanism may involve either supercooling, preferred growth direction or adsorption, but it is not limited by these mechanisms as an explanation of the strengthening

behavior of silver, copper, or gold halides. For each particular metal halide mixture the optimum amount of the strengthening agent is expected to vary within the range from about 0.25 to about 5.0 mole percent, but the present invention is not limited to these composition ranges or to use in the optimum strengthening agent concentration.

The strengthening agent of the present invention may be used as described above in spherical particles, but in certain circumstances it may be advantageous to produce the metal halide particles in cylindrical shapes as by pressing in a die. Silver halides and silver iodide in particular, when added in amounts between about 0.5 and about 5.0 mole percent, have been found to increase the strength of the compacted powders or pellets above that of the powder when silver iodide or silver halide is not added.

Although the strengthening agents can be employed as monoiodides as herein defined, they may also be present as binary mixtures, AgI and CuI, AgI and AuI, and CuI and AuI, and as ternary mixtures, AgI + AuI + CuI, so long as their collective presence in the final metal halide particle is in the range from about 0.25 to about 5.0 mole percent, preferably about 1.0 to about 1.5 mole percent.

While the strengthening agent has been described primarily as a monoiodide, the copper, silver, and gold may also be present as monobromides or monochlorides, in

any combination and in any concentration ratios. In every instance their total presence is desirably between about 0.5 and about 5.0 mole percent, preferably between about 1.0 and 1.5 mole percent.

Although the parent metal halides which are strengthened are generally made from high purity starting materials, i.e., a purity designated as 99.% to 99.999%, the effectiveness of the strengthening agent is not limited to such high purity ranges. Preferably, both the parent metal halide mixture and the strengthening agent are kept with less than 0.05% water content by weight. However, the present invention is not limited by the moisture level of the starting materials.

The strengthening agent may be introduced into the melt or mechanical press as a halide in any solid form, such as spheres, powders, tablets, or pellets, preferably as a finely divided free flowing solid. However, it may also be introduced in solid metallic form, such as silver spheres or silver pellets, and added to the metal halide mixture with a source of halide, e.g.,  $X_2$ ,  $HX$  where  $X$  is  $I$ ,  $Br$  or  $Cl$ .

While a preferred embodiment of the present invention has been described as it relates to vaporizable fill for gas discharge devices, the invention is generally applicable to the strengthening of metal halide pellets or particles and it is to be understood that the embodiments described are illustrative only and the scope of the invention is to be defined solely by the appended

claims when accorded a full range of equivalence, many variations and modifications naturally occurring to those of skill in the art from a perusal hereof.

WHAT IS CLAIMED IS:

1. An improved particle comprising between about 99.5 and 95.0 mole percent of a first metal halide and between about 0.5 and about 5.0 mole percent of a second halide comprising of one or more of halides of gold, silver and copper.

2. Claim 1 where the total hydrogen content of the particle is less than about 20 ppm.

3. Claim 1 wherein the breaking strength of the particle is greater than about 100g.

4. Claim 1 wherein said second metal halide includes a metal from the group consisting of silver or copper and a halide from the group consisting of iodide and bromide;

wherein the total hydrogen content of the particle is less than about 20 ppm;

wherein the total oxygen content of the particle is less than about 50 ppm; and

wherein the breaking strength of the particle is greater than about 250g.

5. An improved Particle comprising:

(a) a parent metal halide from the group consisting of one or more of the following halides:

(i) iodides, (ii) bromides and (iii) chlorides of one or more of the following metals:

Li, Na, K, Rb and Cs in Group 1,

Mg, Ca, Sr and Ba in Group 2,

Sc, Y and La in Group 3,

Ti, Zr and Hf in Group 4,  
Ta and Nb in Group 5,  
Mn in Group 7,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
As, Sb and Bi in Group 15,  
Te in Group 16,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,  
Tm, Yb, and Lu in the Lanthanide Series, and  
Th in the Actinide Series;

(c) a strengthening agent comprising of one or more metal halides from the group consisting of  $\text{AgI}_x$ ,  $\text{AgBr}_x$ ,  $\text{AgCl}_x$ ,  $\text{CuI}_x$ ,  $\text{CuBr}_x$ ,  $\text{CuCl}_x$ ,  $\text{AuI}_x$ ,  $\text{AuBr}_x$  and  $\text{AuCl}_x$  where  $0.95 < x < 1.05$ .

6. The particle of Claim 5 wherein the total oxygen content of the particle is less than about 200 ppm.

7. The particle of Claim 6 wherein the total oxygen content of the particle is less than about 50 ppm.

8. The particle of Claim 5 wherein the total hydrogen content is less than about 100 ppm.

9. The particle of Claim 8 wherein the total hydrogen content is less than about 20 ppm.

10. The particle of Claim 5 wherein the amount of the strengthening agent is between about 0.5 and about 5.0 mole percent.

11. The particle of Claim 10 wherein the amount of the strengthening agent is between about 0.5 and about 1.5 mole percent.

12. The particle of Claim 5 wherein the amount of the strengthening agent is sufficient to increase the breaking strength of the particle without the strengthening agent by a factor of at least 1.25.

13. The particle of Claim 12 wherein the amount of the strengthening agent is sufficient to increase the breaking strength of the particle without the strengthening agent by a factor of about 5.

14. The particle of Claim 13 wherein the amount of the strengthening agent is sufficient to increase the breaking strength of the particle without the strengthening agent by a factor of about 10.

15. The particle of Claim 5 comprising a free-flowing sphere of substantially uniform size and composition with a diameter between about 100 microns and about 3000 microns.

16. The particle of Claim 15 wherein said diameter is between about 150 microns and about 1,200 microns.

17. The particle of Claim 5 wherein said particle is pressurally aggregated.

18. The particle of Claim 5 wherein said particle is generally spherical and has a diameter between about 1600 and about 3000 microns.

19. The particle of Claim 5 wherein said particle has a breaking strength not less than about 150g.

20. The particle of Claim 5 wherein said strengthening agent is one or more of the group consisting of copper monoiodide or silver monoiodide.

21. The particle of Claim 5 wherein the strengthening agent consists of binary mixtures.

22. The particle of Claim 5 wherein the strengthening agent consists of a ternary mixture.

23. The particle of Claim 5 wherein the parent metal halide is not less than about 90 mole percent of the particle.

24. The particle of Claim 5 with a total oxygen content less than about 200 ppm;

with a total hydrogen content less than about 100 ppm;

with a breaking strength greater than about 150g; and

wherein said strengthening agent comprises between about 0.5 and about 5.0 mole percent.

25. The particle of Claim 24 with a total oxygen content less than about 50 ppm;

with a total hydrogen content less than about 20 ppm; and



wherein said strengthening agent comprises between about 1.0 and about 1.5 mole percent.

26. A lamp fill material comprising:

(a) a parent metal halide from the group consisting of one or more of halides from the group consisting of:

(i) iodides, (ii) bromides and (iii) chlorides of one or more of the following metals:

Li, Na, K, Rb and Cs in Group 1,

Mg, Ca, Sr and Ba in Group 2,

Sc, Y and La in Group 3,

Ti, Zr and Hf in Group 4,

Ta and Nb in Group 5,

Mn in Group 7,

Fe in Group 8,

Co in Group 9,

Ni in Group 10,

Zn, Cd and Hg in Group 12,

Al, Ga, In and Tl in Group 13,

Sn and Pb in Group 14,

As, Sb and Bi in Group 15,

Te in Group 16,

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,

Tm, Yb, and Lu in the Lanthanide Series, and

Th in the Actinide Series; and

(b) a strengthening agent comprising one or more metal halides from the group consisting of  $\text{AgI}_x$ ,  $\text{AgBr}_x$ ,  $\text{AgCl}_x$ ,  $\text{CuI}_x$ ,  $\text{CuBr}_x$ ,  $\text{CuCl}_x$ ,  $\text{AuI}_x$ ,  $\text{AuBr}_x$  and  $\text{AuCl}_x$  where  $0.95 < x < 1.05$ .

27. The particle of Claim 26 wherein the total oxygen content of the particle is less than about 200 ppm.

28. The particle of Claim 27 wherein the total oxygen content of the particle is less than about 50 ppm.

29. The particle of Claim 26 wherein the total hydrogen content is less than about 20 ppm.

30. The particle of Claim 29 wherein the total hydrogen content is less than about 5 ppm.

31. The particle of Claim 26 wherein the amount of the strengthening agent is between about 0.5 and about 5.0 mole percent.

32. The particle of Claim 31 wherein the amount of the strengthening agent is between about 0.5 and about 1.5 mole percent.

33. The particle of Claim 26 wherein the parent metal halide comprises not less than about 90 mole percent of the particle.

34. The particle of Claim 26 wherein the amount of the strengthening agent is sufficient to increase the breaking strength of the particle without the strengthening agent by a factor of at least 1.50.

35. The particle of Claim 34 wherein the amount of the strengthening agent is sufficient to increase the breaking strength of the particle without the strengthening agent by a factor of about 10.

36. The particle of Claim 26 wherein said particle has a breaking strength not less than about 100g.

37. The particle of Claim 36 wherein said particle has a breaking strength not less than about 250g.

38. The particle of Claim 37 wherein said particle has a breaking strength not less than about 500g.

39. The particle of Claim 26 comprising a free-flowing sphere of substantially uniform size and composition with a diameter between about 100 microns and about 3000 microns.

40. The particle of Claim 39 wherein said diameter is between about 150 microns and about 1,200 microns.

41. The particle of Claim 26 wherein said particle is pressurally aggregated.

42. The particle of Claim 26 wherein said particle is generally spherical and has a diameter between about 1600 and about 3000 microns.

43. The particle of Claim 26 wherein said particle comprises a mixture of the iodides of dysprosium, neodymium, and cesium with a cesium content above about 35 mole percent.

44. Claim 43 wherein said particle has a breaking strength not less than about 350g.

45. The particle of Claim 26 wherein said parent halide is 70-80 mole percent sodium bromide and 30-20% sodium iodide;

wherein said strengthening agent is 1.5 mole percent silver iodide; and

wherein the breaking strength is not less than about 350g.

46. The particle of Claim 26 wherein the parent halide consists of one or more halides of the group consisting of sodium, scandium and lithium;

wherein the strengthening agent is 1.5 mole percent silver iodide; and

wherein the breaking strength is not less than about 180g.

47. The particle of Claim 26 wherein the parent halide comprises one or more halides of the group comprising tin, thallium and sodium;

wherein the strengthening agent is 1.5 mole percent silver iodide; and

wherein the breaking strength is greater than the breaking strength of the parent halide by a factor greater than three.

48. The particle of Claim 26 wherein the metal in said strengthening agent is one or more of the group consisting of copper and silver.

49. The particle of Claim 48 wherein the metal in said strengthening agent is silver.

50. The particle of Claim 26 wherein the halide in said strengthening agent is an iodide.

51. The particle of Claim 26 wherein said strengthening agent comprises a binary mixture.

52. The particle of Claim 26 wherein said strengthening agent consists of a ternary mixture.

53. The particle of Claim 26 wherein said strengthening agent comprises one or more halides from

the group consisting of iodide and bromide, and one or more metals taken from the group consisting of silver and copper.

54. The particle of Claim 26 wherein said parent metal halide having one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,  
Sc, Y and La in Group 3,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and  
Th in the Actinide Series.

55. The particle of Claim 54 wherein said strengthening agent comprises one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of silver and copper.

56. The particle of Claim 55 wherein the total oxygen content of the particle is less than about 50 ppm;  
and

wherein the total hydrogen content is less than about 5 ppm.

57. The particle of Claim 56 wherein the amount of the strengthening agent is between about 1.0 and about 1.5 mole percent; and

wherein said particle has a breaking strength not less than about 100g.

58. A strengthening agent for a metal halide particle comprising one or more metal halides in the group consisting of  $\text{AgI}_x$ ,  $\text{AgBr}_x$ ,  $\text{AgCl}_x$ ,  $\text{CuI}_x$ ,  $\text{CuBr}_x$ ,  $\text{CuCl}_x$ ,  $\text{AuI}_x$ ,  $\text{AuBr}_x$  and  $\text{AuCl}_x$  where  $0.95 < X < 1.05$ .

59. The agent of Claim 58 wherein the metal is one or more from the group consisting of silver and copper and the halide is taken from the group consisting of iodide and bromide.

60. The agent of Claim 59 wherein the agent is silver iodide.

61. The agent of Claim 58 comprising a monohalide.

62. The agent of Claim 58 comprising a binary mixture.

63. The agent of Claim 58 comprising a ternary mixture.

64. An arc tube for a metal halide lamp including an envelope containing fill material determinative of the electrical and spectral characteristics of the lamp, said material including one or more metals from the group consisting of silver, copper and gold.

65. The arc tube of Claim 64 wherein said metal is contained in one or more metal halide particles.

66. The arc tube of Claim 65 wherein said metal is one or more of the group consisting of gold and copper.

67. The arc tube of Claim 64 wherein the amount of copper, silver and gold halide is less than 1.5 mole percent.

68. An arc tube for a metal halide lamp including an envelope containing fill material determinative of the electrical and spectral characteristics of the lamp, said material including first and second metal halides,

said first metal halide having one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of silver and copper, and

said second metal halide having one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,

Sc, Y and La in Group 3,

Fe in Group 8,

Co in Group 9,

Ni in Group 10,

Zn, Cd and Hg in Group 12,

Al, Ga, In and Tl in Group 13,

Sn and Pb in Group 14,

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and

Lu in the Lanthanide Series, and

Th in the Actinide Series.

69. The arc tube of Claim 68 wherein said fill material contains less than about 5 ppm hydrogen and less than about 20 ppm oxygen.

70. The arc tube of Claim 69 wherein said first halide is between about 1.0 and about 1.5 mole percent.

71. The arc tube of Claim 68 wherein said first metal halide is between about 0.5 and about 5.0 mole percent.

72. The arc tube of Claim 71 wherein said first halide is between about 1.0 and about 1.5 mole percent.

73. A method of strengthening a parent metal halide particle from the group consisting of one or more of the following halides:

- (i) iodides, (ii) bromides, and (iii) chlorides of one or more of the following halides:

Li, Na, K, Rb and Cs in Group 1,  
Mg, Ca, Sr and Ba in Group 2,  
Sc, Y and La in Group 3,  
Ti, Zr and Hf in Group 4,  
Ta and Nb in Group 5,  
Mn in Group 7,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
As, Sb and Bi in Group 15,



Te in Group 16,

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,

Tm, Yb, and Lu in the Lanthanide

Series, and

Th in the Actinide Series

comprising the steps of:

(a) admixing the parent halide with a strengthening agent comprising of one or more metal halides from the group consisting of  $\text{AgI}_x$ ,  $\text{AgBr}_x$ ,  $\text{AgCl}_x$ ,  $\text{CuI}_x$ ,  $\text{CuBr}_x$ ,  $\text{CuCl}_x$ ,  $\text{AuI}_x$ ,  $\text{AuBr}_x$  and  $\text{AuCl}_x$  where  $0.95 < X < 1.05$ ;

(b) melting the admixture; and

(c) forming the particle.

74. The method of Claim 1 wherein the particle is formed by jetting the melt into a cooling tower to form homogeneous spheres of substantially uniform diameter.

75. The method of Claim 1 wherein the particle is formed by the steps of:

(a) freezing the melt to form a solid metal halide.

(b) crushing the solid metal halide; and

(c) pressurally aggregating the crushed metal halide.

76. The method of Claim 1 wherein the particle is formed by dripping the melt into a cooling tower to form homogeneous spheres of substantially uniform diameter between about 1600 microns and about 3000 microns.

77. The method of Claim 1 wherein the particle is formed by casting.

78. The method of Claim 1 wherein said parent metal halide includes one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,

Sc, Y and La in Group 3,

Fe in Group 8,

Co in Group 9,

Ni in Group 10,

Zn, Cd and Hg in Group 12,

Al, Ga, In and Tl in Group 13,

Sn and Pb in Group 14,

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and

Lu in the Lanthanide Series, and

Th in the Actinide Series.

79. The method of Claim 6 wherein the strengthening agent comprises one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of silver and copper.

80. The method of Claim 7 wherein said particle contains less than about 20 ppm hydrogen and less than about 50 ppm oxygen.

81. A method of increasing the strength of a metal halide Particle comprising the steps of:

(a) admixing one or more metal halide salts with one or more metals of the group consisting of silver, gold and copper and a source of a halogen;

(b) melting the admixture; and

(c) forming the melted mixture into a Particle.

82. The method of Claim 9 wherein the metal and the source of halogen are a metal halide.

83. The method of Claim 9 wherein the metal in the metal halide is silver or copper and wherein the halide in the metal halide is iodide or bromide.

84. The method of Claim 9 wherein the amount of the metal halide is between about 0.5 and about 5.0 mole percent.

85. The method of Claim 12 wherein the amount of the metal halide is between about 0.5 and about 1.5 mole percent.

86. The method of Claim 9 wherein the metal halide salt includes one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of silver and copper.

87. The method of Claim 14 wherein said metal halide salt includes one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,

Sc, Y and La in Group 3,

Fe in Group 8,

Co in Group 9,

Ni in Group 10,

Zn, Cd and Hg in Group 12,

Al, Ga, In and Tl in Group 13,

Sn and Pb in Group 14,

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and  
Th in the Actinide Series.

88. The method of Claim 15 wherein said particle contains less than about 20 ppm hydrogen and less than about 50 ppm oxygen.

89. A method of making lamp fill material comprising the steps of:

(a) admixing one or more metal halide salts with one or more metal halides where the metal is from the group consisting of silver, gold and copper and the halide is from the group consisting of iodide, bromide and chloride;

(b) melting the admixture; and

(c) cooling the melted mixture to form a solid lamp fill material.

90. The method of Claim 17 wherein the metal in the metal halide is silver or copper and wherein the halide in the metal halide is iodide or bromide.

91. The method of Claim 18 wherein the amount of the metal halide is between about 0.5 and about 5.0 mole percent.

92. The method of Claim 19 wherein the metal halide salt includes one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,

Sc, Y and La in Group 3,

Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and  
Th in the Actinide Series.

93. The method of Claim 17 wherein said particle contains less than about 20 ppm hydrogen and less than about 50 ppm oxygen.

94. The method of Claim 21 wherein the metal halide is between about 1.0 and about 1.5 mole percent.

95. The method of Claim 17 wherein the metal halide salt includes one or more halides from the group consisting of iodide and bromide, and one or more metals taken from the group consisting of:

Li, Na, K, Rb and Cs in Group 1,  
Sc, Y and La in Group 3,  
Fe in Group 8,  
Co in Group 9,  
Ni in Group 10,  
Zn, Cd and Hg in Group 12,  
Al, Ga, In and Tl in Group 13,  
Sn and Pb in Group 14,  
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
Lu in the Lanthanide Series, and

Th in the Actinide Series.

96. The method of Claim 23 wherein the total hydrogen is less than about 5 ppm and wherein the total oxygen is less than about 20 ppm.



FIG. 1

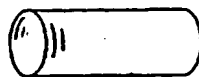


FIG. 2

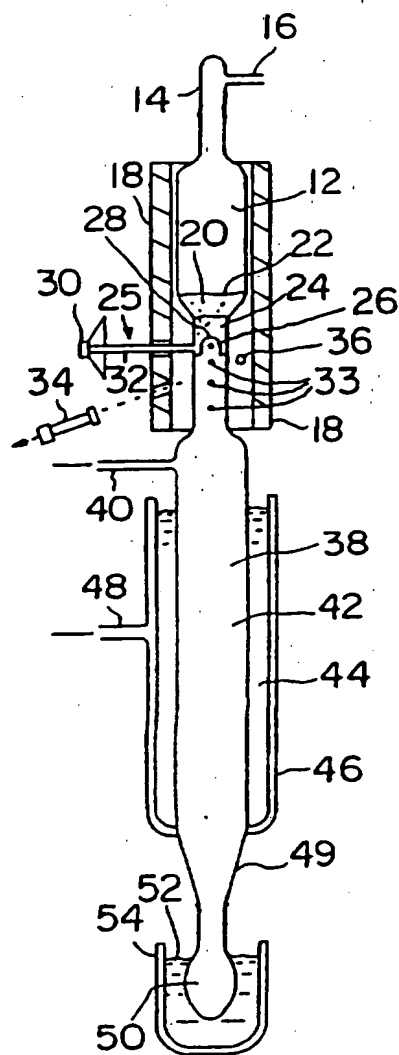


FIG. 3

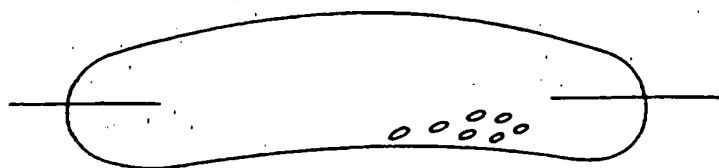
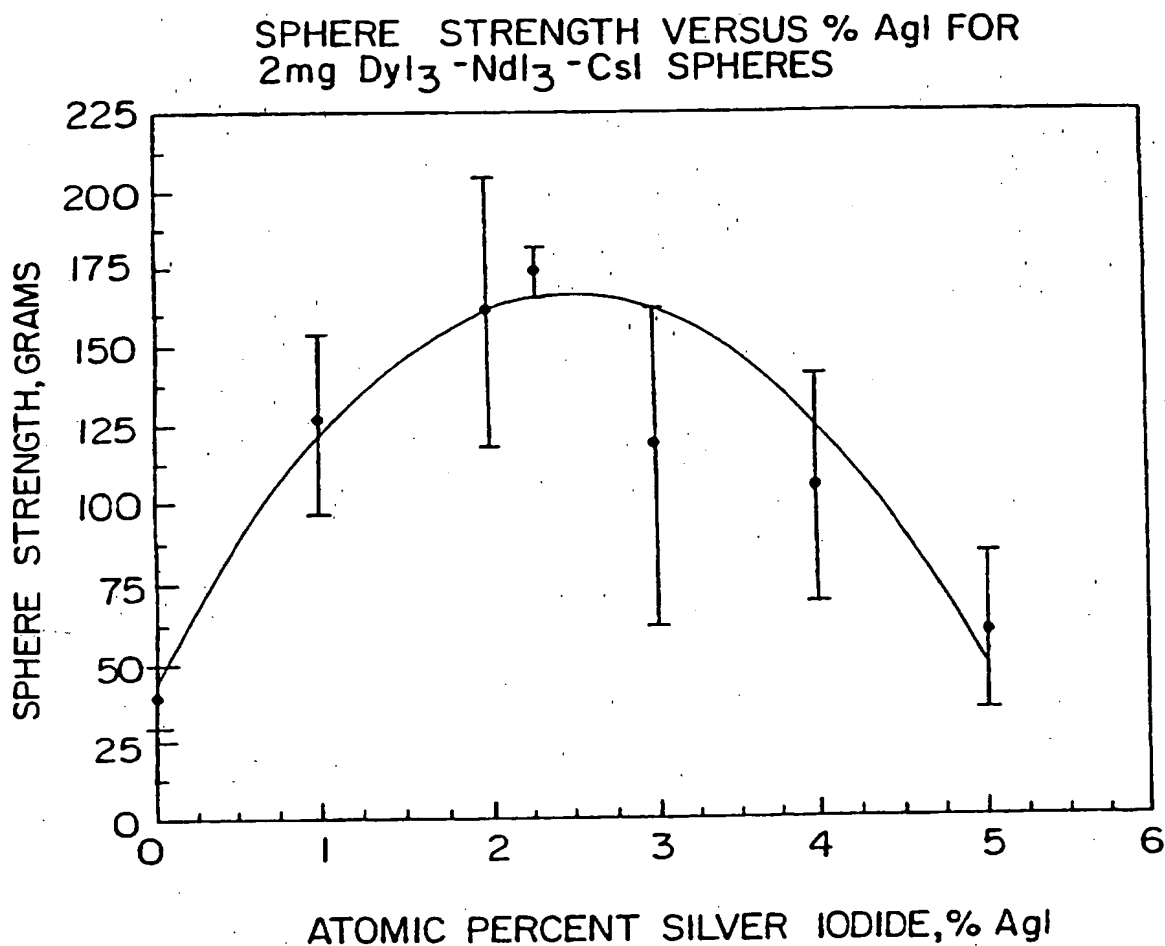


FIG. 4

**FIG. 5**



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/13429

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B22F 1/00; H01J 17/26; B29D 9/10

US CL :75/255; 313/564; 264/5

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 75/255; 313/564; 264/5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,929,869 A (YONEZAWA et al) 29 May 1990, col. 3, lines 49-54.	26, 58-61, 64, 65, 68 ----- 69
Y	US 3,676,534 A (ANDERSON) 11 July 1972, col. 1, lines 61-62.	69

☐

Further documents are listed in the continuation of Box C.

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See patent family annex.

\*

Special categories of cited documents:

\*A\*

document defining the general state of the art which is not considered to be of particular relevance

\*E\*

earlier document published on or after the international filing date

\*L\*

document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\*

document referring to an oral disclosure, use, exhibition or other means

\*P\*

document published prior to the international filing date but later than the priority date claimed

\*T\*

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\*

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\*

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*&amp;\*

document member of the same patent family

Date of the actual completion of the international search

03 SEPTEMBER 1997

Date of mailing of the international search report

07 OCT 1997

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Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/13429

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: metal halide, particles, silver iodide, silver bromide, copper iodide, copper bromide, gas discharge, lamp, arc tube, strengthening agent